



Short communication

Effect of lightweight supports on specific discharge capacity of β -nickel hydroxideT.N. Ramesh^a, R.S. Jayashree^a, P.Vishnu Kamath^{a,*},
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Abstract

While the performance of β_{bc} (bc: badly crystalline)-nickel hydroxide is relatively unaffected by the use of different lightweight supports, the specific discharge capacity of crystalline β -Ni(OH)₂ doubles to approximately 355 mAh g⁻¹ Ni (theoretical, 456 mAh g⁻¹) when pasted to a fibre support compared with 170 mAh g⁻¹ Ni when pasted to a nickel foam. Consequently, the fibre is a superior support as it is unaffected by the quality of the active material and extracts a consistently high performance irrespective of the degree of crystallinity, moisture content, morphology and composition of the active material. Electrochemical impedance measurements indicate that a lower charge-transfer resistance at low states-of-charge is responsible for the superior performance of fibre supported β -Ni(OH)₂ electrodes. © 2002 Published by Elsevier Science B.V.

Keywords: Discharge capacity; Lightweight supports; Foams; Fibres; Nickel hydroxide

1. Introduction

Nickel hydroxide, the positive electrode material of all nickel-based alkaline secondary cells, is a semiconductor with a large band gap [1]. Therefore, electrode fabrication usually consists of bonding the active material to a suitable conducting support. Consequently, two factors contribute to the performance of a working electrode.

1.1. Nature of the support

The support contributes to the weight of the electrode without adding to the capacity, and thus, the gravimetric specific capacity of the electrode is much lower than that of the active material. Therefore, it is of practical interest to develop lightweight supports. Many different supports have been employed, common among these are: sintered nickel porous plaques [2], nickel foams [3] and fibres [4]. Of these, the sintered plaques are the heaviest and constitute nearly 50% of the weight of the electrode. By contrast, foams and fibres are lightweight supports.

1.2. Nature of active material

The most widely used active material is β -nickel hydroxide. The reversible discharge capacity of nickel hydroxide depends on the crystallinity, moisture content and morphology of the material. Badly crystalline β -phases [5] with a high moisture content [6], small particle size [7] and high tap density [8] are known to yield stabilized discharge capacities close to the theoretical value.

Nickel hydroxide is obtained by precipitation from a suitable nickel salt solution using a strong alkali. Among the many factors that affect the outcome of a precipitation reaction, the important ones are the pH at precipitation, temperature and concentration of the solutions, stirring conditions, rate of addition of the reactants, and ageing of the precipitate. To obtain the right combination of physical properties and chemical composition, to yield maximum capacity with an optimum cycle-life, the various process parameters that affect the precipitation reaction have to be delicately controlled. Any variation in the precipitation conditions yields nickel hydroxide of sub-optimal quality which adversely influences the discharge capacity. This study examines whether the nature of the supports used during electrode fabrication determines the performance of the active material and mitigate the effects of its poor quality.

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2. Experimental

Crystalline β -nickel hydroxide was obtained from Aldrich (USA) and used as such. β_{bc} (bc: badly crystalline)-nickel hydroxide was obtained by the addition of aqueous $\text{Ni}(\text{NO}_3)_2$ solution (1 M, 50 ml) to a solution of NaOH (2 M, 100 ml) at 80 °C with constant stirring. The precipitation was completed at a constant, high (>13) pH. The precipitate was filtered immediately, washed free of alkali, and dried to constant weight at 65 °C. The samples were stored without desiccation.

All samples were characterized by powder X-ray diffraction (XRD) (Jeol JDX8P powder diffractometer, Cu K α radiation $\lambda = 1.541 \text{ \AA}$), thermogravimetry (laboratory built system, heating rate, 5 °C min⁻¹), and wet chemical analysis. The sample characteristics are described in detail elsewhere [5].

Nickel foams (NiTech, France) were donated by C. Delmas (France). Nickel fibres were obtained from HBL NIFE Power Systems (Hyderabad, India). Pasted electrodes were fabricated as described elsewhere [5] using both fibre and foam supports. Two electrodes of each variety were prepared to ensure reproducibility of performance. The values of specific discharge capacity reported in this work are normalized to the nickel content of the active material; the theoretical limit for a one e⁻ exchange is 456 mAh g⁻¹.

The electrochemical impedances of the fibre and foam supported nickel hydroxide electrodes were obtained by means of an Eco Chemie Autolab (AUT30) Frequency Response Analyzer (FRA) in the frequency range 10 mHz–10 kHz.

3. Results and discussion

Crystalline β -nickel hydroxide is a stoichiometric material with the chemical composition $\text{Ni}(\text{OH})_2$. It is isostructural with the mineral, brucite $[\text{Mg}(\text{OH})_2]$ and displays sharp

peaks in its XRD pattern. It has a low moisture content of <1%. β_{bc} -nickel hydroxide has a high (up to 12 wt.%) reversible moisture content and exhibits broad peaks in its XRD pattern. In particular, the non-(hk0) peaks have a pronounced broadening [9].

Cycle-life data of crystalline β -Ni(OH)₂ on foam and fibre supports are given in Fig. 1. β -Ni(OH)₂ delivers a stabilized specific discharge capacity of $\sim 170 \text{ mAh g}^{-1}$ Ni which corresponds to a 0.37 e⁻ exchange. This value compares well with that reported by Tesseir et al. [10] on a similar foam support. When the same active material is pasted on a fibre support, however, the stabilized capacity dramatically improves to $\sim 355 \text{ mAh g}^{-1}$, i.e. to a 0.76 e⁻ exchange. Typical discharge curves are given in Fig. 2.

β_{bc} -Nickel hydroxide is known to exhibit a specific discharge capacity of 380 mAh g⁻¹ on foam supports [5]. It was interesting to investigate if pasted electrodes of β_{bc} -nickel hydroxide using fibre supports could provide a similar dramatic increase in performance. Unfortunately, this does not prove to be the case (see Fig. 3).

The beneficial effect of the fibre support on β -nickel hydroxide can be brought about by two mechanisms, namely: (i) the support alters the basic structure and electrochemistry of the active material, (ii) the support provides a superior conducting matrix for the active material. The fact that active materials such as β_{bc} -nickel hydroxide, that perform close to their theoretical limits on foam supports, are unaffected by the use of the fibre implies that the fibre does not alter the structure and the properties of the active material.

The discharge capacity of a nickel hydroxide electrode is limited by the insulating nature of the phase that is formed upon discharge. The highly resistive discharged phase severely restricts material utilization by breaking the electrical contact between particles of the active material. The support plays a critical role in preventing this by providing an effective conducting matrix. To support this conjecture, electrochemical impedance studies have been performed on

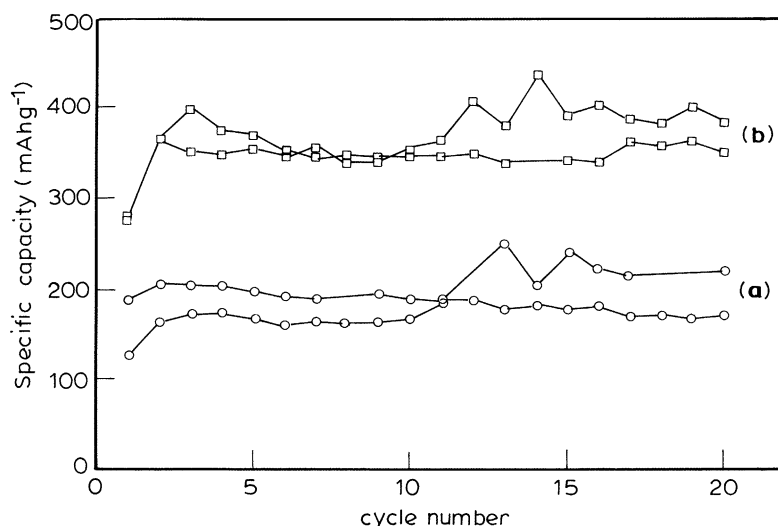


Fig. 1. Cycle-life data of β -Ni(OH)₂ electrodes with (a) foam ; (b) fibre supports.

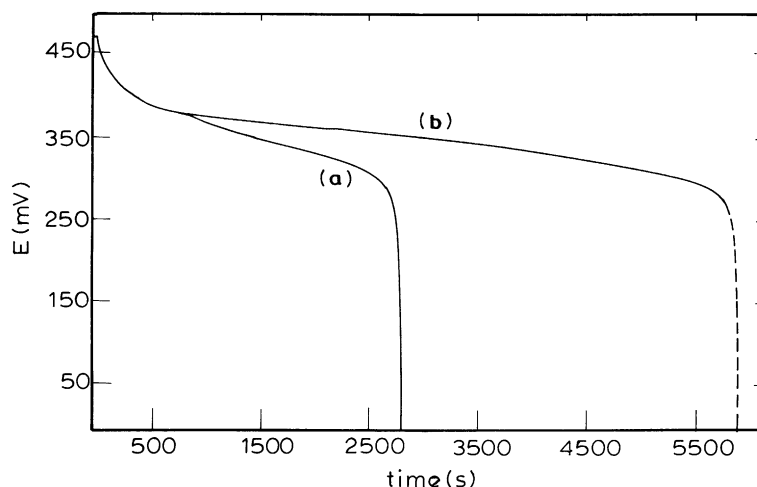


Fig. 2. Discharge profiles (20th cycle) of crystalline nickel hydroxide electrodes fabricated using (a) foam and (b) fibre supports.

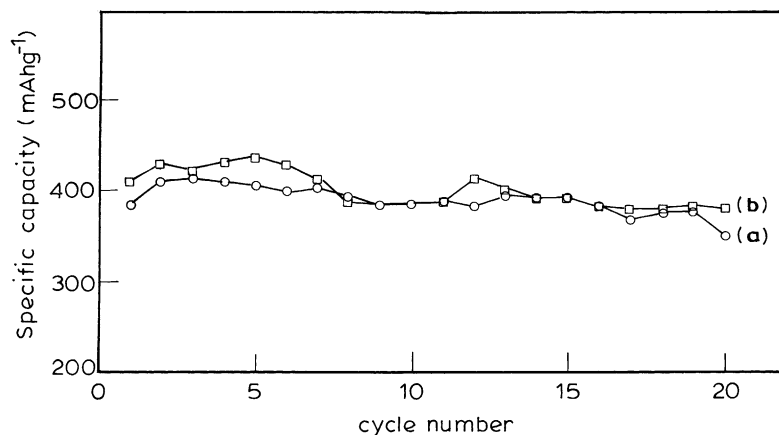


Fig. 3. Cycle-life data of β_{bc} -Ni(OH)₂ electrodes on (a) foam and (b) fibre support.

both fibre and foam supported electrodes. The impedance data were fitted using non-linear square-fitting software supplied with the FRA. The impedance data for the foam and fibre supported electrodes can be fitted to R(RQ) and R(RQ)(RQ) type equivalent circuits where R is the resistive and Q is the capacitive component. The values of solution resistance (R_Ω) and charge-transfer resistance (R_{ct}) are obtained from this analysis at various states-of-charge are given in Table 1.

Table 1

Impedance data for fibre and foam supported β -Ni(OH)₂ electrodes. Values in parentheses correspond to β_{bc} -nickel hydroxide electrodes

SoC*	R_Ω (Ω)		R_{ct} (Ω)	
	Fibre	Foam	Fibre	Foam
1	0.07 (0.10)	0.06 (0.11)	0.14 (0.14)	0.15 (0.14)
0.8	0.11 (0.09)	0.05 (0.09)	0.11 (0.21)	0.11 (0.10)
0.6	0.06 (0.08)	0.03 (0.08)	0.09 (0.13)	0.10 (0.08)
0.4	0.05 (0.07)	0.06 (0.07)	0.10 (0.19)	0.20 (0.14)
0.2	0.07 (0.11)	0.06 (0.09)	0.12 (0.13)	0.16 (0.39)
0	0.05 (1.04)	0.05 (0.07)	3.33 (3.5)	7.5 (5.5)

* State-of-charge.

In the case of β -Ni(OH)₂ electrodes, the R_Ω values are identical at all states-of-charge for both fibre and foam supported electrodes. On the other hand, the R_{ct} values are lower but only at state-of-charge values near zero for the fibre supported electrodes. Accordingly, the fibre supported electrodes permit better material utilization which result in a higher storage capacity in relation to foam-supported electrodes as observed experimentally (Fig. 1).

With β_{bc} -nickel hydroxide electrodes, both R_Ω and R_{ct} are found to be different at state-of-charge values near zero. While the R_{ct} values are smaller for the fibre supported electrodes the R_Ω values are higher than those foam supported electrodes. Therefore, in fibre-supported electrodes, the beneficial effect of the lower R_{ct} value is compensated by the higher R_Ω values. Consequently, both supports result in comparable discharge capacity values as found experimentally (Fig. 3). Nyquist plots at zero state-of-charge for β and β_{bc} -nickel hydroxide electrodes on fibre and foam supports are shown in Figs. 4 and 5, respectively.

A high material utilization can also be obtained by increasing the moisture content, decreasing the particle size

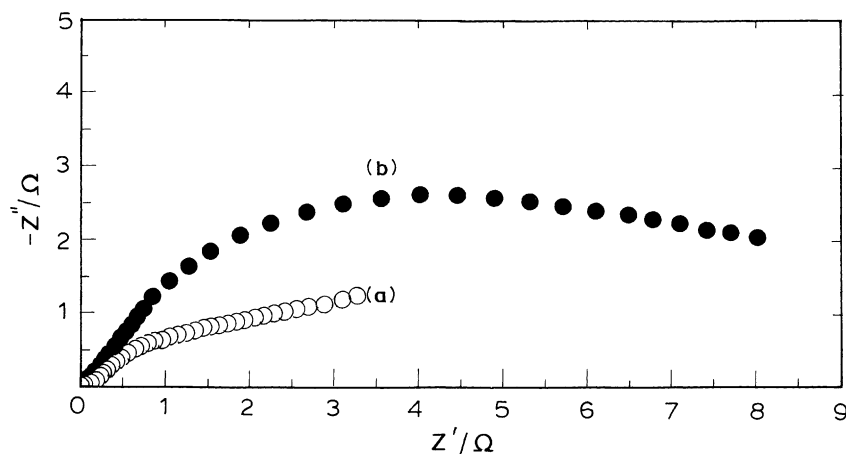


Fig. 4. Nyquist plots for (a) fibre and (b) foam supported β -Ni(OH)₂ electrodes at zero state-of-charge.

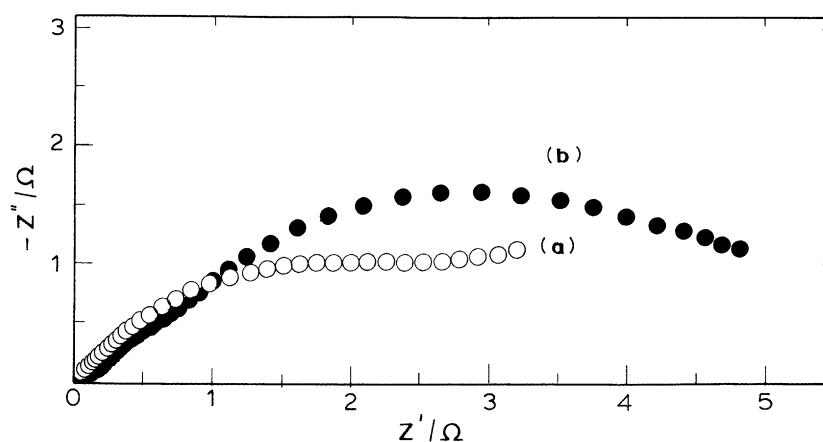


Fig. 5. Nyquist plots for (a) fibre and (b) foam supported β_{hc} -Ni(OH)₂ electrodes at zero state-of-charge.

and increasing the tap density of the active material, but then the synthetic conditions to achieve these characteristics in the active material are demanding. The use of fibre supports compensates for the loss of active material quality more effectively compared to foam supports.

4. Conclusions

Active materials that deliver low reversible discharge capacities on foam supports exhibit a dramatic improvement in their performance when bonded to fibre supports. This establishes fibre-support as the lightweight support of choice for electrode fabrication.

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